

REMARKS

Applicants confirm the election to prosecute claims 4-38, which are designated as Group II in the Restriction Requirement under 35 U.S.C. § 121. In canceling claims 1-3 applicants submit there is no change in inventorship required in the above-identified application.

Applicants respectfully submit the amendment to the specification corrects an obvious incorrect number and minor grammatical errors. Therefore, the amendment does not introduce new matter into the application and should be entered.

Applicants invention comprises two separate and distinct aspects of treating water that are neither taught nor suggested in the prior art cited by the Examiner, namely:

- "1) The use using a mixture of chlorine dioxide and chlorine to treat water, and
- 2) The use of a mixture of chlorine dioxide and monochloramine to treat water."

The two aspects of the invention are intimately related in that a novel chlorine dioxide-monochloramine mixture may be formed by adding ammonia to the chlorine dioxide-chlorine mixture. For the reasons that will follow Applicants respectfully submit that the use of such mixtures are neither taught nor suggested in the prior art.

Generally, the chlorine-chlorine dioxide mixture is best applied to water with relatively low to moderate THMFP (trihalomethanes formation potential)-for example, in low demand raw water and finished water. The chlorine dioxide-chloramine mixture is best applied to water with relatively high THMFP.

The application of the chlorine-chorine dioxide mixture may achieve greater disinfection (a higher total CxT) than the application of either chlorine or chlorine dioxide alone, while staying within the DBP (disinfection by-product) limits

for THM, HAA and chlorite ion. This is because each of the oxidants have different, individually regulated DBPs, but their CxT "credits" may be additive. Further, the phenomenon of "chlorite ion recycling" affords maintenance of a higher chlorine dioxide residual, without increasing the applied chlorine dioxide dose. This facilitates a higher chlorine dioxide CxT credit without an increase in residual chlorite ion, a regulated DBP. The application of the chlorine dioxide-monochloramine mixture can achieve high-level, rapid oxidation/disinfection while simultaneously achieving persistent, long-lasting, low level oxidation and disinfection.

The sequential application of these mixtures to water treatment-e.g., by starting with the chlorine-chlorine dioxide mixture, and then converting it into the chlorine dioxide-chloramine (by the addition of ammonia) may under some circumstances be especially advantageous.

The ability to utilize a mixture of chlorine and chlorine dioxide adds the economic advantage of being able to use less expensive generation techniques-e.g., HCI and sodium chlorate-that previously had been rejected <u>because</u> they generate mixtures of chlorine and chlorine dioxide.

The application of various oxidants, including chlorine dioxide, chlorine, and monochloramine, is well known in the art of water treatment. But oxychlorine chemistry is complex. One can't simply assume that oxychlorine compounds, in mixture, will behave as they do individually. They usually don't. Related oxychlorine species that can play important roles in water treatment applications include chlorine dioxide (ClO_2), monochloramine (NH_2Cl), dichloramine ($NHCl_2$), nitrogen trichloride (NCl_2), chlorine (Cl_2), chlorite ion (ClO_2), chlorate ion (ClO_3), perchlorate ion (ClO_4), chlorous acid ($HClO_2$) hypochlorite ion (OCl), and hypochlorous acid (HOCl). On mixing (in water), these species can react with each other and even with the water itself. The extent and nature of the reaction(s) are determined by, among other things, the absolute and relative concentrations of the reactants, pH, temperature, and the presence of other chemicals.

It should be noted that ozone (O_3) is another oxidant used in water treatment. Certain features of ozone chemistry may help underscore the point that

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just because an oxidant can be used individually to treat water, it doesn't necessarily follow that it can also be used in mixture with other oxidants.

Each oxidant used in water treatment has its own, unique set of associated disinfection by-products (DBPs), many of which are regulated. Chlorine forms THMs and HAAs in reaction with organics. Ozone forms aldehydes, carboxylic acids and bromate ion (from bromide ion). Chlorine dioxide use results in chlorite ion and chlorate ion. Since ~50-70% of applied dose of chlorine dioxide winds up as chlorite ion, the MCL (regulated limit) of 1ppm for chlorite ion effectively limits the applied dose of chlorine dioxide to a maximum 1.4ppm.

Each oxidant used in water treatment also has a unique set of capabilities for killing target organisms. The relative hierarchy may change, depending on the organism being targeted. The ability to kill microbes is inversely proportional to its "required CxT" value. That is, the lower the required CxT, the more effective the disinfectant. The CxT for ozone (the strongest of the chemical disinfectants) vis-à-vis Cryptosporidium parvum (a waterborne pathogenic parasite) is lower than that for chlorine dioxide, which is lower than that for chlorine, which is lower than that for chloramines (the weakest of the chemical disinfectants). Yet, chlorine and chlorine dioxide are comparably effective against viruses. The task of achieving necessary levels of disinfection/oxidation, while complying with DBP regulations, is a major challenge to water treaters. Part of the value of the subject invention is that it helps water treaters to balance the conflicting requirements (DBP limits vs disinfection/oxidation requirements) and better meet that challenge.

High oxidant demand and THM "formation potential" (THMFP) are usually, but not always, coincident. For example, if water has a low organics content but very high metals content (iron, manganese), the oxidant demand would be high, but the THMFP would be low. Generally, the oxidant demand and THMFP decrease as the water progresses through treatment steps. This information may be useful in understanding why the two mixtures of the subject invention may more or less advantageously applied at different treatment points, and may sometimes be advantageously converted from the first to the second, in the course of the water treatment process.

The Examiner has rejected claim 12 under 35 U.S.C. § 103(a) over Griese et al. U.S. Patent 5,314,629 in view of Hurst U.S. Patent 4,693,832.

Contrary to the allegation of the Examiner neither Griese et al. or Hurst teach applying a mixture of chlorine and chlorine dioxide to treat the water. Both references refer to water treatment by sequential application of chlorine and chlorine dioxide. The references above or combined do not teach or suggest applying a mixture of chlorine and chlorine dioxide at the same location during the water treatment process. It is respectfully submitted that the art of water treatment is replete with teachings that explicitly reject the use of a mixture of chlorine and chlorine dioxide in water treatment and in point of fact rely upon using the various oxidants, e.g. chlorine-chlorine dioxide ozone and monochloramine sequentially in the treatment of drinking water.

It is well known that chlorine-chlorine dioxide, ozone and monochloramine are applied <u>sequentially</u> in various combinations in the treatment of drinking water. However, the art teaches against any of these oxidants, and especially against chlorine dioxide, being mixed with other oxidants. In the case of chlorine dioxide, the art teaches against both <u>generation</u> of a mixture and also against application of a mixture, to wit:

From George Clifford White's Handbook of Chlorination and Alternative Disinfectants, 4th Ed., (1998) the following information is relevant to understanding the prior art that was available when Applicants made their invention.

<u>Chapter 12. Chlorine Dioxide (pp 1134)</u> there is a specific admonition against mixing chlorine dioxide with other oxidants:

"never mix chlorine dioxide with other oxidants (e.g., ozone)"

<u>Chapter 12. Chlorine Dioxide (pp 1159-1160)</u> argues for a standard for chlorine dioxide "Purity", limiting the aggregate amount of free chlorine, chlorite ion and chlorate ion in chlorine dioxide (being used for drinking water treatment). The author proposes a "procurement specification" based on said Purity standard, limiting the total aggregate amount of free chlorine, chlorite ion and chlorate ion in chlorine

dioxide to a maximum of 1% by weight. In the most extreme case, this would permit a maximum chlorine content of 1% by weight.

<u>Chapter 12. Chlorine Dioxide (pp 1169-1170)</u> reviews chlorine dioxide production methods. Notwithstanding potential economic advantages, it rejects certain sodium chlorate based methods owing to chlorine content of the chlorine dioxide product:

"The prospect of being able to use a much-lower-cost feedstock to produce chlorine dioxide (i.e., sodium chlorate vs. sodium chlorite) is enticing...Attempts... have combined concentrated acid such as hydrochloric with sodium chlorate...". The chemistry is wholly unsatisfactory...as it produces an effluent with severely depressed pH that tends to contain high chlorine-impurity levels."

For example, in the USEPA Guidance Manual (1999):

<u>Chapter 4. Chlorine Dioxide §4.4.2 Chlorine Dioxide Purity</u>, teaches against the presence of chlorine in the generated chlorine dioxide:

"Chlorine dioxide generators are operated to obtain the maximum production (yield) of chlorine dioxide, while minimizing free chlorine or other residual oxidant formation... In addition, the measurable excess chlorine should be less than 2 percent by weight in the generator effluent."

Chapter 9. Combined Disinfectants. §9.1.6 Chlorine/Chlorine to Chlorine Dioxide/Chlorine, teaches against the presence of excess chlorine in the chlorine dioxide feed stream:

"Use of chlorine dioxide as a pre-oxidant to replace chlorine may allow moving the point of chlorination downstream in the process train for application to water with lower NOM (natural organic matter) concentrations. The reduced precursor concentration and the reduced chlorine dose should result in a reduction of chlorinated DBPs. However, if excess chlorine is present in the chlorine dioxide feed stream, it would react with NOM prior to removal in sedimentation and filtration if pre-oxidation is practiced"

Chapter 9. Combined Disinfectants, §9.2 Pathogen Inactivation with Interactive Disinfectants, discusses both sequential application of oxidants, as well as application of "combinations". EPA's discussion of combinations (mixtures) was limited to: (a) free chlorine and organic N-halamine, (b) free chlorine and sodium bromide, and (c) chloramine and cupric chloride. Chlorine-chlorine dioxide, ozone and monochloramines are never discussed in mixture with each other, but only vis-à-vis sequential application:

"...Research on interactive disinfectants for primary pathogen inactivation is under way for several combinations of disinfectants:

Chlorine followed by chloramine;
Chlorine dioxide followed by chlorine;
Chlorine dioxide followed by chlorine dioxide;
Chlorine dioxide followed by chloramine;
Ozone followed by chlorine;
Ozone followed by chlorine dioxide; and
Ozone followed by chloramine."

Also:

Chapter 9. Combined Disinfectants. §9.1.3 Chlorine/Chlorine to Chlorine/Chloramine, teaches against the presence of excess free chlorine in mixture with monochloramines: Excess free chlorine in the presence of a mixture of monochloramine and chlorine dioxide will also produce dichloramine and trichloramine (a/k/a nitrogen trichloride). This highlights the complexity and sensitivity of monochloramine-formation chemistry.)

"...the ammonia/chlorine mixing conditions should be optimized to quickly remove free chlorine from the system

<u>Chapter 9. Combined Disinfectants. §9.1.4 Chlorine/Chlorine to</u>

<u>Ozone/Chlorine</u>, teaches against the mixing of ozone and chlorine. (This highlights the fact that, just because an oxidant can be used individually, it doesn't necessarily follow that it can also be used in mixture with other oxidants.)

"...ozone should be completely decomposed or chemically quenched prior to chlorine addition. If ozone is present when chlorine is added, the ozone will react with the chlorine and NOM (define NOM) present to form chlorinated DPBs..."

For example, from www.clo2.com, the website of Sterling Pulp Chemicals, a leading worldwide supplier of chlorine dioxide technology, and one of the world's largest producers of sodium chlorate and sodium chlorite, one finds a teaching against combining ammonia with chlorine dioxide (http://www.clo2.com/factsheet/safety.html):

"Reactive Chemical Hazards: Chlorine dioxide is incompatible with ammonia..."

In view of the foregoing it is respectfully submitted that the Examiner has used Applicants own teaching to not only select but to interpret the prior art, which is clearly contrary to existing Patent Law.

Neither Griese et al. nor Hurst alone or in combination teach the use of a mixture of chlorine and chlorine dioxide in a primary water treatment process, wherein the mixture either as a gas or in solution is injected into the water where the point of injection is after THM precursors are removed from the water such that the level of chlorinated bi-products created is within acceptable limits. Therefore, in view of the foregoing it is respectfully submitted that the rejection of claim 12 under 35 U.S.C. § 103(a) is not well taken and should be withdrawn.

The Examiner has rejected claims 22-28 and 30 under 35 U.S.C. § 103(a) over Griese et al. in view of Harp et al. U.S. Patent 6,315,950.

For the reasons set forth above it is respectfully submitted that Griese et al. neither teaches nor suggests using a <u>mixture of chlorine and chlorine dioxide</u> to treat the water. Furthermore, neither Griese et al. alone or Harp et al. alone or in combination teach or suggest the use of injecting a <u>mixture</u> of chlorine dioxide and monochloramine into raw water to cause pre-oxidation by chlorine dioxide and introduction of monochloramine into the water as it proceeds through subsequent processing steps while treating the water after solid removal with a <u>mixture</u> of

chlorine dioxide and chlorine or a mixture of chlorine dioxide chlorine and ammonia for final disinfection.

Here again, the Examiner is using Applicant's own teaching to not only select but to interpret the prior art, clearly contrary to existing Patent Law. For the reasons pointed out above by the art none of the references can be interpreted individually or in combination to teach or suggest that mixtures of chlorine and chlorine dioxide should be used in treating water. This is further reinforced by the fact that in view of the more current art, as reflected by the teaching in the Handbook of Chlorination and Alternative Disinfection, the USEPA Guidance Manual and the Sterling Pulp Chemicals Web Site, the processes of Griese et al. would not be modified by the teaching of Harp et al. since the current technology is to do other than suggested by Applicants invention. In point of fact, the new art teaching the cited prior art can be interpreted to these processes that are directly opposite to those of the present invention. Only when using Applicant's teaching is used to interpret the prior art can the Rejection seem viable. Again this clearly contrary to existing Patent Law.

Therefore, it is respectfully submitted that the rejection of claims 22-28 and 30 under 35 U.S.C. § 103(a) is not well taken and should be withdrawn.

It cannot be too strongly argued that the processes of the present invention are not merely process optimization and the use of pretreated side streams is a novel addition to the otherwise novel and unobvious basic process.

The Examiner has rejected claims 4-11, 18-21, 29 and 30 under 35 U.S.C. § 103(a) over Griese et al. in view of Hurst further in view of Harp et al.

While adding chlorine to ammonia or ammonia to chlorine to form monochloramine is known in the prior art what is not known and unobvious is that the process of the present invention begins with a <u>chlorine-chlorine dioxide mixture</u> resulting in forming chloramines by reacting the chlorine with ammonia in the presence of chlorine dioxide and utilizing a mixture of chloramines and chlorine dioxide, which is clearly neither taught nor suggested by the prior art. Here again,

the Examiner is using Applicants own teaching to not only select but to interpret the references, which is clearly contrary to existing Patent Law.

Since the basic process of the invention is neither taught nor suggested by the prior art, the sub steps of the present invention cannot be considered obvious over the prior art.

Again, Applicants refer to the discussion above concerning the prohibition in the art of using chlorine-chorine dioxide mixtures in water treatment and the fact that they have utilized chlorine-chlorine dioxide mixtures with and without ammonia to provide effective water treatment processes.

Therefore, it is respectfully submitted that the rejection of claims 4-11, 18-21, 29 and 31 under 35 U.S.C. § 103(a) is not well taken and should be withdrawn.

The Examiner has rejected claims 13 and 15 under 35 U.S.C. § 103(a) over Griese et al. in view of Glew et al. U.S. Patent 4,137,296.

For the reasons set forth above it is respectfully submitted that the teaching of Griese et al. neither teaches nor suggests the processes of the present invention, which have at their core using mixtures of chlorine and chlorine dioxide or chlorine dioxide and chloramines. While the generation of mixtures of chlorine and chlorine dioxide and the separation thereafter of the components are well known in industry, especially in the pulp and paper industry, no one has taught or suggested using a chlorine-chlorine dioxide mixture for water treatment. Therefore, there is no teaching in the water treatment processes of the prior art of separating chlorine-chlorine dioxide mixtures into its constituent chlorine dioxide and chlorine components.

Here again, the claims set forth the process by starting with the <u>mixture</u> of chlorine-chlorine dioxide and separating the stream so that the chlorine and chlorine dioxide can be used in various parts of the overall water treatment process. Here again since the use of a chlorine-chlorine dioxide mixture in water

treatment is strongly taught against by the prior art, one would not start with such mixtures which can then be separated into components of a water treatment process.

In view of the foregoing it is respectfully submitted that the rejection of claims 13 and 15 under 35 U.S.C. § 103(a) is not well taken and should be withdrawn.

The Examiner has rejected claims 14, 16 and 17 under 35 U.S.C. § 103(a) over Griese et al. in view of Glew et al. and further in view of Harp et al. Here again, there is no argument with the fact that addition of chlorine to ammonia or ammonia to chlorine is a method by which chloramines can be produced. However, what is not taught nor suggested by the prior art and what is new is the processes of the present invention that start with a chlorine dioxide-chlorine mixture and then and form chloramines by reacting chlorine with ammonia in the presence of chlorine dioxide and utilizing mixtures of chloramines and chlorine dioxide in the claimed processes to treat the water. For the reasons set forth above it is respectfully submitted that the prior art would lead one to concluding that the use of chlorine-chlorine dioxide mixtures are undesirable in providing effective water treatment. Applicants have shown that the use of a chlorine-chlorine dioxide mixture which can be separated into various fractions and used in various parts of the water treatment process with or without the addition of ammonia to result in a mixture of chlorine dioxide and chloramine is neither taught nor suggested by the prior art. Here again the Examiner is using Applicant's teaching to not only select but to interpret the prior art, which is clearly contrary to existing Patent Law.

Therefore, it is respectfully submitted that the rejection of claims 14, 16 and 17 under 35 U.S.C. § 103(a) is not well taken and should be withdrawn.

The Examiner has rejected claims 32, 34 and 37 under 35 U.S.C. § 103(a) over Griese et al. in view of Glew et al. further in view of Rosenblatt et al. Patent No. (not specified).

Contrary to the interpretation by the Examiner, Rosenblatt et al. teaches separation of a chlorine dioxide effluent stream from a reactor stream that may contain residual chlorine gas. The product of the reactor is passed through a

scrubber to remove any residual chlorine prior to the application of the chlorine dioxide for the intended purpose. The use of the scrubber is to remove trace amounts of chlorine gas contaminant from a system designed to produce substantially pure chlorine dioxide. Contrast this with the present invention which intentionally starts with a chlorine-chlorine dioxide mixture, which is then processed in various ways to provide components for treatment of water to make it potable. The chlorine is not scrubbed from the mixture but is an integral and useful part of the mixture used in Applicant's process.

Here again, Applicants refer to the above discussion concerning the fact that the accepted prior art suggests that mixtures of chlorine and chlorine dioxide should not be used in water treatment. Once again if Applicant's teaching is divorced from the prior art, it neither teaches nor suggests that the use of chlorine-chlorine dioxide mixtures can be the starting point for effective water treatment.

In view of the foregoing it is respectfully submitted that the rejection of claims 32, 34 and 37 under 35 U.S.C. § 103(a) is not well taken and should be withdrawn.

The Examiner has rejected claims 33, 35, 36 and 38 under 35 U.S.C. § 103(a) over Griese et al. in view of Glew et al. and Rosenblatt et al. further in view of Harp et al.

For the reasons set forth above, it is respectfully submitted that the references either alone or in combination neither teach nor suggest the present invention which resides in starting with a chlorine dioxide-chlorine <u>mixture</u>, forming chloramines by reacting chlorine with the ammonia in the presence of chlorine dioxide, and utilizing a <u>mixture</u> of chloramines and chlorine dioxide to provide an effective water treatment process.

Here again, for the reasons set forth above, the prior art neither teaches nor suggests starting with a chlorine dioxide-chlorine <u>mixture</u> and in point of fact teaches away from using such a mixture as a starting point. Once the Applicants teaching is divorced from the prior art there is neither a teaching nor a suggestion of Applicants process from the art cited by the Examiner.

In view of the foregoing it is respectfully submitted that the rejection of claims 33, 35, 36 and 38 under 35 U.S.C. § 103(a) is not well taken and should be withdrawn.

The Examiner has shown no motivation in any of the combinations proposed in rejecting Applicants claim that would lead a worker skilled in the art to make the assumptions and reach the conclusions set forth by the Examiner without using Applicants own teaching in interpreting the prior art and in formulating a process or processes taught by the present invention.

Once again, Applicants respectfully submit that the Examiner has fallen into the trap of using their teaching to not only select but to interpret the prior art. Clearly the prior art neither teaches nor suggest a water treatment process that is based upon the use of chlorine-chlorine dioxide mixtures or mixtures of chlorine dioxide and monochloramine to provide effective water treatment resulting in a potable water.

In view of the foregoing amendments and arguments it is respectfully submitted that the above-identified application is in condition for allowance and a notice to that effect is earnestly solicited.

Respectfully Submitted,

Attorney for Applicants

JCS/mc

Enclosures:

Version with markings to show changes made

Dated: January 14, 2003

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James C Symmon



VERSION WITH MARKINGS TO SHOW CHANGES MADE

SPECIFICATION:

Specification at page 15, line 18:

In this case, as shown in Figure 7 chlorine dioxide and/or chloramine may be added at the entrance to the finished water storage 34-134 as shown by arrow 196. Since the finished water typically has low chlorine dioxide demand, and the retention time in the finished water storage 134 is typically long, a relatively low dose of chlorine dioxide in the finished water may provide adequate CxT for primary disinfection, even if the monochloramine remaining from injection in the raw water is not adequate. Monochloramine injected into the finished water storage will mostly be carried on as a residual in the distribution system.

CLAIMS:

Please cancel claims 1-3 without prejudice to applicant's right to file a divisional application thereon.

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